

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2001-200151**

(43)Date of publication of application : **24.07.2001**

(51)Int.Cl.

C08L 69/00

C08J 5/00

C08K 5/5399

// (C08L 69/00

C08L 85:02

C08L 83:04)

(21)Application number : **2000-006667** (71)Applicant : **OTSUKA CHEM CO LTD**

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(54) FLAME-RETARDANT POLYCARBONATE RESIN COMPOSITION AND MOLDED BODIES THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polycarbonate resin composition that has a high degree of flame retardancy occurring no burn-melt dripping without adverse effect on the high transparency and the mechanical strengths that are intrinsically excellent properties of aromatic polycarbonate.

SOLUTION: The objective aromatic polycarbonate resin composition is obtained by formulating (B) 0.1-40 pts.wt. of at least one phenoxyphosphazene selected from cyclic phenoxyphosphazenes, chain phenoxyphosphazenes and crosslinkable phenoxyphosphazenes and (C) 0.01-50 pts.wt. of at least one compound selected from organic alkali metal salts, organic alkaline earth metal salts and organopolysiloxanes to (A) 100 pts.wt. of an aromatic polycarbonate resin.

LEGAL STATUS

[Date of request for examination] 05.06.2000

[Date of sending the examiner's decision of rejection] 08.05.2002

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]	
[Patent number]	3605719
[Date of registration]	15.10.2004
[Number of appeal against examiner's decision of rejection]	2002-010305
[Date of requesting appeal against examiner's decision of rejection]	07.06.2002
[Date of extinction of right]	

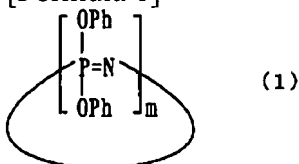
CLAIMS

[Claim(s)]

[Claim 1] (A) The fire-resistant polycarbonate resin constituent characterized by the thing which is chosen as at least one sort of phenoxy phosphazene compounds 0.1 chosen as the aromatic series polycarbonate resin 100 weight section from (B) annular phenoxy phosphazene compound, the chain-like phenoxy phosphazene compound, and the bridge formation phenoxy phosphazene compound - 40 weight sections list from (C) organic alkali-metal salt, an organic alkaline-earth-metal salt, and organopolysiloxane, and which blended at least one sort of 0.01 - 50 weight sections.

[Claim 2] (B) The annular phenoxy phosphazene compound of a component is a general formula (1).

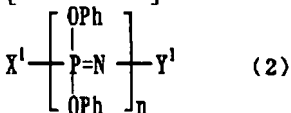
[Formula 1]



The integer of 3-25 is shown by the inside m of [type. Ph shows a phenyl group.] The fire-resistant polycarbonate resin constituent according to claim 1 which is annular phenoxy phosphazene come out of and expressed.

[Claim 3] (B) The chain-like phenoxy phosphazene compound of a component is a general formula (2).

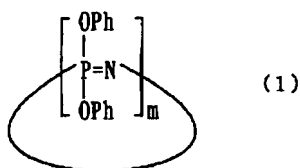
[Formula 2]



Radical-N=P (OPh)3 or radical-N=P(O) OPh is shown by the inside X1 of [type, and Y1 is a radical. - P(OPh) 4 or radical-P(O) (OPh)2 are shown. n shows the integer of 3-10000. Ph is the same as the above.] The fire-resistant polycarbonate resin constituent according to claim 1 which is chain-like phenoxy phosphazene come out of and expressed.

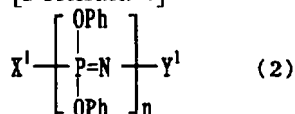
[Claim 4] (B) The bridge formation phenoxy phosphazene compound of a component is a general formula (1).

[Formula 3]



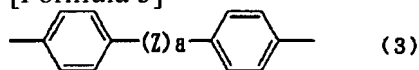
The integer of 3-25 is shown by the inside m of [type. Ph shows a phenyl group.] The annular phenoxy phosphazene and the general formula (2) which are come out of and expressed

[Formula 4]



Radical-N=P (OPh)₃ or radical-N=P(O) OPh is shown by the inside X¹ of [type, and Y¹ is a radical. - P(OPh)₄ or radical-P(O) (OPh)₂ are shown. n shows the integer of 3-10000. Ph is the same as the above.] At least one sort of phosphazene compounds chosen from the group which comes out and consists of chain-like phenoxy phosphazene expressed are o-phenylene group, m-phenylene group, p-phenylene group, and a general formula (3).

[Formula 5]



-C(CH₃)₂-, -SO₂-, -S-, or -O- is shown by the inside Z of [type. a shows 0 or 1.] It is the compound over which at least one sort of bridge formation radicals chosen from the group which comes out and consists of a bis-phenylene group expressed come to construct a bridge. (a) This bridge formation radical intervenes between two oxygen atoms from which the phenyl group of a phosphazene compound was desorbed. (b) The content percentage of a phenyl group is 50 - 99.9% on the basis of the total of the above-mentioned phosphazene compound (1) and/or all the phenyl groups in (2). And the fire-resistant polycarbonate resin constituent according to claim 1 which is a bridge formation phenoxy phosphazene compound which does not have the free hydroxyl group in (c) intramolecular.

[Claim 5] (C) The fire-resistant polycarbonate resin constituent according to claim 1 whose organic alkali-metal salt and organic alkaline-earth-metal salt of a component are at least one sort chosen from the alkali-metal salt of an organic sulfonic acid, the alkali-metal salt of organophosphate, the alkali-metal salt of an organic carboxylic acid, the alkaline-earth-metal salt of an organic sulfonic acid, the alkaline-earth-metal salt of organophosphate, and the alkaline-earth-metal salt of an organic carboxylic acid.

[Claim 6] (C) The fire-resistant polycarbonate resin constituent according to claim 1 whose organopolysiloxane of a component is a phenyl content siloxane compound.

[Claim 7] Claim 1, claim 2, claim 3, claim 4, the fire-resistant polycarbonate resin Plastic solid that can fabricate and obtain a fire-resistant polycarbonate resin constituent according to claim 5 or 6.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a fire-resistant polycarbonate resin constituent. Furthermore, this invention relates to the polycarbonate resin constituent which has the advanced fire retardancy which does not show the dropping phenomenon at the time of combustion in detail, without aromatic series polycarbonate resin spoiling the transparency and the mechanical physical properties which it originally has.

[0002]

[Description of the Prior Art] Aromatic series polycarbonate resin is excellent in a mechanical strength (especially impact property-proof), electrical characteristics, transparency, etc., and is broadly used in the field with various electrical-and-electric-equipment fields, an automobile and the machine field, construction fields, etc. The field of which advanced fire retardancy is required focusing on OA equipment and the electrical-and-electric-equipment field is in these fields of the invention.

[0003] Aromatic series polycarbonate resin has a high oxygen index in various thermoplastics, and although it is resin which generally has self-extinguishing, in order to fill the demand OA equipment, the electrical-and-electric-equipment field, and on insurance [in / in addition to this / various applications], it is required that the description of the transparency which raising fire retardancy further and aromatic series polycarbonate resin originally have should be held.

[0004] Conventionally, various kinds of approaches of blending an organic halogenide, and organic or an inorganic sulfonate are learned as the flameproofing approach of aromatic series polycarbonate resin.

[0005] How to specifically blend deca BUROMO diphenyloxide with aromatic series polycarbonate resin (JP,54-52152,A), How to blend with aromatic series polycarbonate resin the aromatic series polycarbonate of a 2 and 2-bis(4-hydroxy - 3, 5-dibromo phenyl) propane (= tetrabromobisphenol A) by which the end blockade was carried out with the halogenation phenol (JP,47-41422,B), The approach (JP,47-24660,B, JP,47-44537,B, JP,55-25466,A) of adding the oligomer of tetrabromobisphenol A to aromatic series polycarbonate resin is learned. However, these approaches have the fault which the thermal stability at the time of shaping falls since the halogenated compound is added, and generates corrosive thru/or toxic gas and smoke at the time of shaping or combustion.

[0006] moreover, generally, if an organic halogenide is used together with antimony oxide compounds (for example, an antimony trioxide, sodium antimonate, etc.), at the time of combustion, halogenation antimony is generated, a front face is covered, continuation of combustion is checked, raising fire retardancy is known, and this technique is applied widely ("-- fifth edition" -- reference, such as publication Maruzen Co., Ltd. edited by the Chemical Society of Japan, (1995), II, and the 423rd page). [edited by chemistry handbook applied chemistry] However, even when an organic halogenide and an antimony oxide compound are used together, the fault which there is no change in having added the halogenated compound, and the thermal stability at the time of shaping falls like the above, and generates corrosive thru/or toxic gas and smoke at the time of shaping or combustion arises.

[0007] moreover, the approach (JP,47-40445,B --) of blending the alkali-metal salt of perfluoro alkane sulfonate with aromatic series polycarbonate resin JP,54-32456,B, the

approach of blending the metal salt of an aromatic series sulfonamide (JP,56-45945,B), How to blend the metal salt of an aliphatic series ether sulfonic acid (JP,54-106562,B), the approach (JP,57-28424,B --) of blending the metal salt of an aromatic series sulfonic acid The approach (JP,54-68857,A, JP,55-27303,A) of blending JP,58-43099,B, JP,58-13587,B, and the sulfate metal salt of alcohols is indicated. However, by these approaches, the aromatic series (about 1.5mm in for example, thickness) polycarbonate resin mold goods which have the advanced fire retardancy which all does not show a dropping phenomenon at the time of combustion and which carried out thinning are not obtained. In order to acquire fire retardancy sufficient with these compounds, spoiling the transparency which is a property which needed to carry out abundant addition and excelled [resin] in aromatic series polycarbonate resin, and becoming opaque is not avoided.

[0008] Moreover, although the method (JP,60-38418,B) of preventing dropping at the time of combustion by mixing an organic alkali-metal salt and an alkaline earth metal salt to an aromatic series polycarbonate, and adding polytetrafluoroethylene further is indicated, in this technique, there is a fault that the transparency which is the original description of an aromatic series polycarbonate is spoiled.

[0009] Furthermore, it is the compound (JP,7-41653,A) with which organophosphate was also known from the former as a flame retarder. Although transparency is held even if it carries out abundant addition at aromatic series polycarbonate resin, in order for this organophosphate to satisfy fire retardancy, there is an inclination for resin to be plasticized by add organophosphate so much, heat deflection temperature becomes low, and mechanical properties, such as shock resistance, get worse. On the other hand, in order to take out fire retardancy effectively by addition of little organophosphate, the approach of adding the poly fluoroalkane, for example, polytetrafluoroethylene, further for the purpose of the dropping prevention at the time of combustion is learned (JP,59-36657,B, JP,6-45747,B). However, it is unescapable that the transparency of an aromatic series polycarbonate is lost by addition of polytetrafluoroethylene by this approach.

[0010] On the other hand, in order to improve the fire retardancy of aromatic series polycarbonate resin, the approach of copolymerizing a polysiloxane in an aromatic series polycarbonate or the approach of adding silicone resin is learned. For example, in order to obtain fire-resistant polycarbonate resin, the approach (JP,63-289059,A, JP,1-210462,A, JP,4-202465,A) of using the mixture of an aromatic series polycarbonate-organopolysiloxane copolymer or an aromatic series polycarbonate-organopolysiloxane copolymer, and aromatic series polycarbonate resin is learned. However, the polycarbonate resin which whose aromatic series polycarbonate-organopolysiloxane copolymer independent fire-resistant engine performance is still inadequate, and was excellent in fire retardancy is not yet obtained.

[0011] Moreover, in order to obtain a flame-retardant-resin constituent, the approach (JP,62-60421,B, JP,63-31513,B, JP,3-48947,B, JP,6-128434,A, JP,7-78171,B, JP,7-33971,A, JP,10-139964,A, JP,11-140294,A) of blending various silicone resin with aromatic series polycarbonate resin is indicated. However, the above-mentioned siloxane copolymer or the compound which has siloxane structure like silicone resin cannot demonstrate effective fire-resistant effectiveness, unless the flameproofing effectiveness is small and adds so much. if the addition is made [many] in order to acquire sufficient fire retardancy -- many physical properties, such as the moldability of a resin constituent,

an appearance of mold goods, and a mechanical strength, -- large -- not falling -- since it does not obtain and silicone resin is used so much, it is not avoided that the resin constituent itself becomes expensive. Moreover, the dispersibility and compatibility of silicone resin to aromatic series polycarbonate resin are not enough, two components from which a refractive index differs in a moldings carry out phase separation, and there is also a problem that do not become low [transparency] or only a thing opaque when there are many loadings is obtained.

[0012] Therefore, the physical characteristic and optical transparency of aromatic series polycarbonate resin are maintained, and development of the technique which gives usable cheap and advanced fire retardancy to the application of the large range is desired.

[0013]

[Problem(s) to be Solved by the Invention] This invention makes it a technical problem to offer the polycarbonate resin constituent which has the advanced fire retardancy which does not show the dropping phenomenon at the time of combustion, without aromatic series polycarbonate resin spoiling the transparency and the mechanical property which it originally has.

[0014]

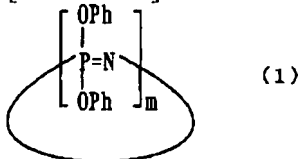
[Means for Solving the Problem] In order that this invention person may solve the above-mentioned technical problem, as a result of repeating research wholeheartedly, in the (A) aromatic series polycarbonate resin 100 weight section (B) In at least one sort of phenoxy phosphazene compounds 0.1 chosen from the annular phenoxy phosphazene compound, the chain-like phenoxy phosphazene compound, and the bridge formation phenoxy phosphazene compound - 40 weight sections list, (C) organic alkali-metal salt, It found out that the resin constituent which is chosen from an organic alkaline-earth-metal salt and organopolysiloxane and which comes to blend at least one sort of 0.01 - 50 weight sections could turn into a desired fire-resistant polycarbonate resin constituent. This invention is completed based on this knowledge.

[0015] That is, this invention is a fire-resistant polycarbonate resin constituent which is chosen as at least one sort of phenoxy phosphazene compounds 0.1 chosen as the 1.(A) aromatic series polycarbonate resin 100 weight section from (B) annular phenoxy phosphazene compound, the chain-like phenoxy phosphazene compound, and the bridge formation phenoxy phosphazene compound - 40 weight sections list from (C) organic alkali-metal salt, an organic alkaline-earth-metal salt, and organopolysiloxane and which comes to blend at least one sort of 0.01 - 50 weight sections.

2.(B) The annular phenoxy phosphazene compound of a component is a general formula (1).

[0016]

[Formula 6]

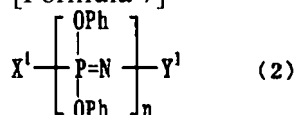


[0017] The integer of 3-25 is shown by the inside m of [type. Ph shows a phenyl group.] The fire-resistant polycarbonate resin constituent of one above-mentioned publication which is annular phenoxy phosphazene come out of and expressed.

3.(B) The chain-like phenoxy phosphazene compound of a component is a general formula (2).

[0018]

[Formula 7]

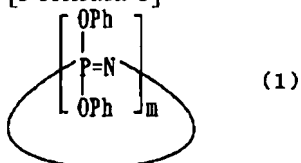


[0019] Radical-N=P (OPh)₃ or radical-N=P(O) OPh is shown by the inside X1 of [type, and Y1 is a radical. - P(OPh)₄ or radical-P(O) (OPh)₂ are shown. n shows the integer of 3-10000. Ph is the same as the above.] The fire-resistant polycarbonate resin constituent of one above-mentioned publication which is chain-like phenoxy phosphazene come out of and expressed.

4.(B) The bridge formation phenoxy phosphazene compound of a component is a general formula (1).

[0020]

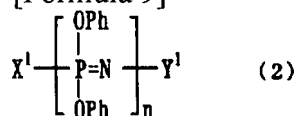
[Formula 8]



[0021] The integer of 3-25 is shown by the inside m of [type. Ph shows a phenyl group.] The annular phenoxy phosphazene and the general formula (2) which are come out of and expressed

[0022]

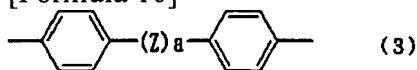
[Formula 9]



[0023] Radical-N=P (OPh)₃ or radical-N=P(O) OPh is shown by the inside X1 of [type, and Y1 is a radical. - P(OPh)₄ or radical-P(O) (OPh)₂ are shown. n shows the integer of 3-10000. Ph is the same as the above.] At least one sort of phosphazene compounds chosen from the group which comes out and consists of chain-like phenoxy phosphazene expressed are o-phenylene group, m-phenylene group, p-phenylene group, and a general formula (3).

[0024]

[Formula 10]



[0025] -C(CH₃)₂-, -SO₂-, -S-, or -O- is shown by the inside Z of [type. a shows 0 or 1.] It is the compound over which at least one sort of bridge formation radicals chosen from the group which comes out and consists of a bis-phenylene group expressed come to construct a bridge. (a) This bridge formation radical intervenes between two oxygen

atoms from which the phenyl group of a phosphazene compound was desorbed. (b) The content percentage of a phenyl group is 50 - 99.9% on the basis of the total of the above-mentioned phosphazene compound (1) and/or all the phenyl groups in (2). And a fire-resistant polycarbonate resin constituent given in the above 1 which is the bridge formation phenoxy phosphazene compound which does not have the free hydroxyl group in (c) intramolecular.

5.(C) Fire-resistant polycarbonate resin constituent of one above-mentioned publication whose organic alkali-metal salt and organic alkaline-earth-metal salt of component are at least one sort chosen from alkali-metal salt of organic sulfonic acid, alkali-metal salt of organophosphate, alkali-metal salt of organic carboxylic acid, alkaline-earth-metal salt of organic sulfonic acid, alkaline-earth-metal salt of organophosphate, and alkaline-earth-metal salt of organic carboxylic acid.

6.(C) Fire-resistant polycarbonate resin constituent of one above-mentioned publication whose organopolysiloxane of component is phenyl content siloxane compound.

7. Fire-resistant polycarbonate resin Plastic solid which can fabricate and obtain fire-resistant polycarbonate resin constituent of publication to the above 1, 2, 3, 4, and 5 or 6. [0026] The polycarbonate resin constituent which has the advanced fire retardancy which does not show the dropping phenomenon at the time of combustion is offered without aromatic series polycarbonate resin spoiling the transparency and the mechanical properties (for example, shock resistance, dimensional stability, thermal stability, etc.) which it originally has according to this invention.

[0027]

[Embodiment of the Invention] (A) It is the thermoplastic aromatic series polycarbonate polymer or copolymer which is obtained by making carbonyl halide or carbonic acid diester react in an aromatic series dihydroxy compound, or this and a little polyhydroxy compound as aromatic series polycarbonate resin of the (A) component used for component this invention and which may branch.

[0028] As an aromatic series dihydroxy compound, a well-known thing can be used widely conventionally. When the typical example of an aromatic series dihydroxy compound is given, a 2 and 2-bis(4-hydroxyphenyl) propane (= bisphenol A), A 2 and 2-bis(3, 5-dibromo-4-hydroxyphenyl) propane (= tetrabromobisphenol A), Bis(4-hydroxyphenyl) methane, 1, and 1-bis(4-hydroxyphenyl) ethane, A 2 and 2-bis(4-hydroxyphenyl) butane, 2, and 2-bis(4-hydroxyphenyl) octane, A 2 and 2-bis(4-hydroxy-3-methylphenyl) propane, 1, and 1-bis(3-t-butyl-4-hydroxyphenyl) propane, A 2 and 2-bis(4-hydroxy - 3, 5-dimethylphenyl) propane, A 2 and 2-bis(3-BUROMO-4-hydroxyphenyl) propane, 2, and 2-bis(3, 5-dichloro-4-hydroxyphenyl) propane, A 2 and 2-bis(3-phenyl-4-hydroxyphenyl) propane, A 2 and 2-bis(3-cyclohexyl-4-hydroxyphenyl) propane, 1 and 1-screw (bis(hydroxy aryl) alkanes; 1 illustrated by 4-hydroxyphenyl-1-phenyl ethane, bis(4-hydroxyphenyl) diphenylmethane, etc., and a 1-bis(4-hydroxyphenyl) cyclopentane --) The bis(hydroxy aryl) cycloalkanes illustrated by a 1 and 1-bis(4-hydroxyphenyl) cyclohexane etc.; 4 and 4'-dihydroxy diphenyl ether, Dihydroxy diaryl ether illustrated with 4, 4'-dihydroxy -3, 3'-dimethyl diphenyl ether, etc.; 4 A 4'-dihydroxydiphenyl sulfide, The dihydroxy diaryl sulfides illustrated by 4, 4'-dihydroxy -3, a 3'-dimethyl diphenyl sulfide, etc.; 4 A 4'-dihydroxydiphenyl sulfoxide, The dihydroxy diaryl sulfoxides illustrated by 4, 4'-dihydroxy -3, a 3'-dimethyl diphenyl sulfoxide, etc.; 4 4'-dihydroxy diphenylsulfone, 4 and 4'-dihydroxy -3, dihydroxy diaryl

sulfones; hydroquinone [which is illustrated by - dimethyl diphenylsulfone etc.], resorcinol, and 3',4',4'-dihydroxydiphenyl, etc. are mentioned.

[0029] In this invention, these aromatic series dihydroxy compounds are independent, or two or more sorts may use them, mixing. In these aromatic series dihydroxy compound, a bis(4-hydroxyphenyl) alkane system especially 2, and 2-bis(4-hydroxyphenyl) propane is used suitably.

[0030] Moreover, in this invention, to the above-mentioned aromatic series dihydroxy compound, a polyhydroxy compound can be used together as a branching-ized agent in [0.01-3 mol] %, and can also be made into a branching-ized polycarbonate. As a polyhydroxy compound, a well-known thing can be used widely conventionally. For example, a FURORO glycine, 2, 6-dimethyl - 2, 4, a 6-Tori (4-hydroxyphenyl)-3-heptene, 4, 6-dimethyl - 2, 4, a 6-Tori (4-hydroxyphenyl)-2-heptene, 1, 3, 5-Tori (2-hydroxyphenyl) benzole, 1 and 1, 1-Tori (4-hydroxyphenyl) ethane, two -- six - a screw (2-hydroxy-5-methylbenzyl) - four - methyl phenol -- alpha -- alpha -- ' -- alpha -- " - Tori (4-hydroxyphenyl) - the polyhydroxy compound illustrated with 1, 3, and 5-triisopropyl benzene etc. is mentioned.

[0031] Moreover, as carbonyl halide or carbonic acid diester, a well-known thing can be used widely conventionally, and dialkyl carbonate, such as diaryl carbonate and dimethyl carbonate, such as a phosgene and diphenyl carbonate, and diethyl carbonate, etc. is specifically mentioned.

[0032] Generally the viscosity average molecular weight converted from the methylene-chloride solution viscosity in 25 degrees C of aromatic series polycarbonate resin is 15,000-60,000 preferably on 10,000-100,000, shaping, or the physical properties of mold goods.

[0033] In this invention, it faces manufacturing the aromatic series polycarbonate resin which has such viscosity average molecular weight, and the catalyst for promoting a suitable molecular weight modifier and a suitable reaction etc. can also be added if needed. As the monovalence aromatic series hydroxy compound suitable for adjusting molecular weight, Specifically, halogenation objects, such as alkylation objects, such as a phenol, m-methyl phenol, p-methyl phenol, m-propyl phenol, p-propyl phenol, p-tert-butylphenol, p-tert-octyl phenol, p-cumyl phenol, and a p-long-chain alkylation phenol, and p-bromine phenol, etc. are mentioned.

[0034] The aromatic series polycarbonate resin of the (A) component used by this invention may be independent one sort, and what was mixed two or more sorts is sufficient as it.

(B) The phenoxy phosphazene compound of the (B) component used as a flame retarder in component this invention is at least one sort chosen from the annular phenoxy phosphazene compound, the chain-like phenoxy phosphazene compound, and the bridge formation phenoxy phosphazene compound. As such a phenoxy phosphazene compound, a well-known thing can be used widely conventionally.

[0035] As an annular phenoxy phosphazene compound, the annular phenoxy phosphazene compound expressed with the above-mentioned general formula (1), for example can be mentioned.

[0036] As a chain-like phenoxy phosphazene compound, the chain-like phenoxy phosphazene compound expressed with the above-mentioned general formula (2), for example can be mentioned.

[0037] As a bridge formation phenoxy phosphazene compound For example, at least one sort of phosphazene compounds chosen from the group which consists of chain-like phenoxy phosphazene expressed with the annular phenoxy phosphazene and the general formula (2) which are expressed with the above-mentioned general formula (1) It is the compound over which at least one sort of bridge formation radicals chosen from the group which consists of a bis-phenylene group expressed with o-phenylene group, m-phenylene group, p-phenylene group, and the above-mentioned general formula (3) come to construct a bridge. (a) This bridge formation radical intervenes between two oxygen atoms from which the phenyl group of a phosphazene compound was desorbed. (b) The content rate of a phenyl group can mention the bridge formation phenoxy phosphazene compound which is 50 - 99.9% and does not have the free hydroxyl group in (c) intramolecular on the basis of the total of the above-mentioned phosphazene compound (1) and/or all the phenyl groups in (2).

[0038] (B) Also in the phenoxy phosphazene compound of a component, a bridge formation phenoxy phosphazene compound is suitable.

[0039] In this invention, "not having a free hydroxyl group in a molecule" means that the free amount of hydroxyl groups is below limit of detection, when a quantum is carried out [page / of an analytical chemistry handbook / 353rd / (the 3rd edition of revision, edited by Japan Society for Analytical Chemistry, Maruzen Co., Ltd., 1981)] according to the acetylating method by the acetic anhydride and pyridine of a publication. Limit of detection is the limit of detection as a hydroxyl equivalent per 1g (bridge formation phenoxy phosphazene compound of this invention) of samples, and is more specifically below 1×10^{-6} hydroxyl equivalent / g here.

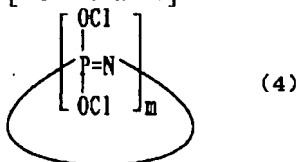
[0040] In addition, if the bridge formation phenoxy phosphazene compound of this invention is analyzed by the above-mentioned acetylation approach, the amount of the hydroxyl group of the raw material phenol which remains will also be added, but since a raw material phenol can carry out a quantum with high performance chromatography, the quantum only of the free hydroxyl group in a bridge formation phenoxy phosphazene compound can be carried out.

[0041] The annular phenoxy phosphazene compound and chain-like phenoxy phosphazene compound which are used by this invention are a known compound.

[0042] The bridge formation phenoxy phosphazene compound of this invention is also a well-known compound, for example, it is a general formula (4).

[0043]

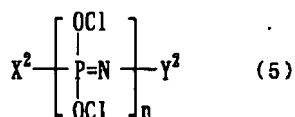
[Formula 11]



[0044] It is the same as the above the inside m of [type.] The annular dichlorophosphazene and the general formula (5) which are come out of and expressed

[0045]

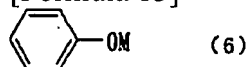
[Formula 12]



[0046] Radical-N=PCl₃ or radical-N=P(O) Cl is shown by the inside X₂ of [type, and Y₂ is a radical. - PCl₄ or radical-P(O) Cl₂ is shown. n is the same as the above.] To at least one sort of dichlorophosphazene compounds chosen from the group which comes out and consists of straight chain-like dichlorophosphazene expressed, it is a general formula (6).

[0047]

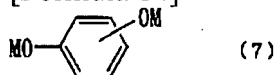
[Formula 13]



[0048] Alkali metal is shown by the inside M of [type.] The alkali-metal phenolate come out of and expressed, and a general formula (7)

[0049]

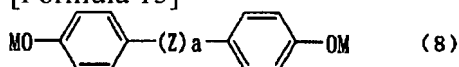
[Formula 14]



[0050] It is the same as the above the inside M of [type.] Alkali-metal JIFENORATO and the general formula (8) which are come out of and expressed

[0051]

[Formula 15]



[0052] It is the same as the above the inside Z, a, and M of [type.] It is manufactured by what you make mixture with at least one sort of JIFENORATO chosen from the group which comes out and consists of alkali-metal JIFENORATO expressed react (the first process), and is made for the above-mentioned alkali-metal phenolate to react to the compound subsequently obtained further (the second process).

[0053] The dichlorophosphazene compound expressed with the general formula (4) and general formula (5) which are used as one of the raw materials in the above-mentioned manufacturing method For example, JP,57-87427,A, JP,58-19604,B, JP,61-1363,B, JP,62-20124,B, H, R, Allcock work, "Phosphorus-Nitrogen Compounds", Academic Press, (1972), J.E.M ark, H.R.Allcock, R.West work, "Inorganic Polymers"Prentice-Hall According to the well-known approach of a publication (1992), it can manufacture to International, Inc., etc.

[0054] If the example is shown, first, in chlorobenzene or tetrachloroethane, an ammonium chloride and a phosphorus pentachloride (or an ammonium chloride, a phosphorus trichloride, and chlorine) are made to react at about 120-130 degrees C, and the dichlorophosphazene compound expressed with the general formula (5) the dichlorophosphazene compound expressed with the general formula (4) whose m is 3-25, and whose n are 3-25 can be manufactured by carrying out demineralization oxidization. These dichlorophosphazene compounds (dichlorophosphazene oligomer) are usually obtained as mixture.

[0055] Moreover, one can manufacture the dichlorophosphazene compound expressed with the general formula (5) which are 25-10000 by heating and carrying out ring opening polymerization of annular dichlorophosphazene compounds, such as hexachlorocyclotriphosphazene, octachlorocyclotetraphosphazene, and deca KURORU cyclopentaphosphazene, and the hexachlorocyclotriphosphazene to 220-250 degrees C with distillation or recrystallization from the dichlorophosphazene oligomer mixture of the shape of annular [which was obtained by doing in this way], and a chain.

[0056] With the dichlorophosphazene of the shape of annular and a chain mixed, it may dissociate and the dichlorophosphazene compound manufactured above may be used independently respectively.

[0057] As an alkali-metal phenolate expressed with a general formula (6), a well-known thing can be used widely conventionally, for example, a sodium phenolate, a potassium phenolate, a lithium phenolate, etc. can be mentioned. These alkali-metal phenolate can use one sort independently, or can use two or more sorts together.

[0058] In alkali-metal JIFENORATO expressed with a general formula (7), two radical-OM (M is the same as the above) may be in alt.* meta or which physical relationship of Para. As an example of this alkali-metal JIFENORATO, alkali-metal salts, such as resorcinol, hydroquinone, and a catechol, can be mentioned, for example. Also in these, sodium salt and lithium salt are desirable. This alkali-metal JIFENORATO can use one sort independently, or can use two or more sorts together.

[0059] As alkali-metal JIFENORATO expressed with a general formula (8), alkali-metal salts, such as - oxydi phenol, and - sulfonyl diphenol (bisphenol - S), and 4 and 4'-isopropylidene diphenol (bisphenol A), 4, and 4 '4, 4'-thiodiphenol, 4, and 4 '4, 4'-diphenol, etc. can be mentioned, for example. Also in these, sodium salt and lithium salt are desirable. This alkali-metal JIFENORATO can use one sort independently, or can use two or more sorts together.

[0060] In this invention, alkali-metal JIFENORATO expressed with alkali-metal JIFENORATO and the general formula (8) which are expressed with a general formula (7) may be used independently, respectively, and these may be mixed and used.

[0061] In the first process of the manufacturing method of this invention, it is desirable to adjust the amount of an alkali-metal phenolate and the alkali-metal JIFENORATO used so that the chlorine atom in a dichlorophosphazene compound may not be altogether consumed by the reaction with an alkali-metal phenolate and alkali-metal JIFENORATO, namely, as the chlorine atom in a dichlorophosphazene compound remains in addition also by the reaction with an alkali-metal phenolate and alkali-metal JIFENORATO. Thereby, both-OM radical (M is the same as the above) of alkali-metal JIFENORATO combines with the Lynn atom of a dichlorophosphazene compound. What is necessary is just to usually make preferably about 0.05-0.9Eq of the amount of an alkali-metal phenolate and the alkali-metal JIFENORATO used into about 0.1-0.8Eq with the total quantity of both phenolates on the basis of the chlorinity of a dichlorophosphazene compound at the first process.

[0062] In the second process of the manufacturing method of this invention, it is desirable to adjust the amount of the alkali-metal phenolate used so that all of all of the chlorine atom and the free hydroxyl group in the compound generated at the first process of the above may be consumed by the reaction with an alkali-metal phenolate. What is necessary is just to usually make preferably about 1-1.5Eq of the amount of the alkali-

metal phenolate used into about 1-1.2Eq on the basis of the chlorinity of a dichlorophosphazene compound in this invention.

[0063] this invention -- the operating rate (alkali-metal JIFENORATO / alkali-metal phenolate, mole ratio) of an alkali-metal phenolate (total quantity used at the first process and the second process), and alkali-metal JIFENORATO -- usually -- about 1 / 2000 to 1/4 -- desirable -- 1 / 20 - 1/6 -- then, it is good.

[0064] the reaction of the first process and the second process -- each usual room temperature - it is preferably carried out to the bottom of the temperature of about 80-140 degrees C, and about 150 degrees C is usually completed preferably in about 3 - 7 hours for about 1 to 12 hours. Each reaction of the first process and the second process is usually performed in organic solvents, such as halogenated-aromatics hydrocarbons, such as aromatic hydrocarbon, such as benzene, toluene, and a xylene, mono-chlorobenzene, and dichlorobenzene.

[0065] The bridge formation phenoxy phosphazene compound of this invention manufactured by the above-mentioned reaction follows the usual isolation approaches, such as washing, filtration, and desiccation, and can be easily isolated and refined from a reaction mixture.

[0066] The bridge formation phenoxy phosphazene compound of this invention has decomposition temperature in within the limits which is 250-350 degrees C.

[0067] Moreover, the content percentage of the phenyl group in the bridge formation phenoxy phosphazene compound of this invention is 50 - 99.9% on the basis of the total of all the phenyl groups in the annular phenoxy phosphazene of a general formula (1), and/or the straight chain-like phenoxy phosphazene of a general formula (2), and is 70 - 90% preferably.

[0068] in addition, when the end groups X1 and Y1 in a general formula (2) change with reaction conditions etc., and are the usual reaction conditions, for example, a mild reaction is performed by the system of non-water X1 becomes $-N=P(OPh)_3$ and Y1 becomes the structure of $-P(OPh)_4$. When it reacts by severe reaction condition which is a reaction condition to which moisture or an alkali-metal hydroxide exists in the system of reaction, or a transition reaction produces X1 will be in the condition that X1 other than the structure of $-P(OPh)_4$ is intermingled by $-N=P(OPh)_3$ and Y1, and the thing of the structure of $-P(O)(OPh)_2$ is intermingled by $-N=P(O)OPh$ and Y1.

[0069] The loadings of the phenoxy phosphazene compound which is the (B) component in this invention need to be within the limits of 0.1 - 40 weight section to the component 100 weight section (above-mentioned [A]). (B) When fire-resistant effectiveness is not demonstrated when there are few loadings of the phenoxy phosphazene compound which is a component than the 0.1 weight section, but 40 weight sections are exceeded conversely, cause the machine physical-properties fall of the aromatic series polycarbonate resin Plastic solid acquired. As for the loadings of the phenoxy phosphazene compound which is the (B) component in this invention, it is desirable to consider as the range of 0.3 - 20 weight section to the component 100 weight section (above-mentioned [A]).

[0070] In this invention, in case annular [of the (B) component], the shape of a chain, and a bridge formation phenoxy phosphazene compound decompose or burn, they do not generate harmful gas or smoke to a living thing, such as hydrogen halide, and do not start the corrosion of metal mold, degradation of resin, and coloring from not containing

halogens, such as chlorine and a bromine, at the time of resin shaping. Moreover, the phenoxy phosphazene compound of this invention does not reduce the molding temperature of resin, and its volatility is low and it does not have blocking or that ooze out (JUSHINGU) and problems, such as dripping at the time of combustion, arise at the time of kneading.

[0071] Moreover, since the bridge formation phenoxy phosphazene compound of this invention is a bridge formation phenoxy phosphazene compound which does not have the one end hydroxy group of a dihydroxy compound substantially, it does not reduce the molecular weight of aromatic series polycarbonate resin, and does not reduce the properties of resin original, such as mechanical properties, such as shock resistance, thermal resistance, fabrication nature, and transparency.

(C) In component this invention, at least one sort chosen from an organic alkali-metal salt, an organic alkaline-earth-metal salt, and organopolysiloxane is used as a (C) component.

[0072] As an organic alkali-metal salt or an organic alkaline-earth-metal salt, although various kinds of things are known, by this invention, at least one sort chosen from the alkali-metal salt of the organic acid which has at least one carbon atom, or organic-acid ester, or the alkaline-earth-metal salt is used.

[0073] Here, it may be an organic sulfonic acid, an organic carboxylic acid, organophosphate, etc., and a halogen like a fluorine, chlorine, and a bromine may be permuted and the ester of an organic acid or an organic acid may be oligomer or a polymer further. As oligomer and a polymer, a polymer, oligomer, etc. which have a sulfonyl group, a carboxyl group, a phospho group, etc. can be mentioned, for example to the intramolecular of polymers, such as polystyrene, or oligomer.

[0074] As an organic sulfonic acid, for example 1-propane sulfonic acid, 1-hexane sulfonic acid, And aliphatic series sulfonic acids, such as a 3-(2-methoxyethoxy)-1-propane sulfonic acid, A 1 and 1-difluoro-1-butane sulfonic acid, 1 and 1, a 2-trifluoro-4-methoxy-1-butane sulfonic acid, A 1, 1, 2, 3, 3, and 3-hexafluoro-1-propane sulfonic acid, Perfluoro methansulfonic acid, perfluoro ethane sulfonic acid, a perfluoro propane sulfonic acid, a perfluoro butane sulfonic acid, a perfluoro methyl butane sulfonic acid, a perfluoro hexane sulfonic acid, a perfluoro heptane sulfonic acid, And fluorine-containing alkane sulfonic acids, such as perfluorooctane sulfonate, Benzenesulfonic acid, p-iodobenzene sulfonic acid, naphthalene -2, 6-disulfonic acid, A naphthalene tris RUHON acid, 2, 5-dichlorobenzene sulfonic acid, 3, 4-dichlorobenzene sulfonic acid, 2 and 4, 5-trichlorobenzene sulfonic acid, A 4 and 4'-dibromo diphenyl-3-sulfonic acid, 2, 3, 4 and 5, a 6-PENTA chloro-beta-styrene sulfonic acid, A 4 and 4'-dichloro diphenyl sulfide-3-sulfonic acid, a tetra-chlorodiphenyl ether disulfon acid, 4, the 4'-dichloro benzophenone -3, a 3'-disulfon acid, 2, a 5-dichloro thiophene-3-sulfonic acid, A diphenylsulfone-3-sulfonic acid, diphenylsulfone -3, a 3'-disulfon acid, 2, 4, 6-TORIKURORO-5-sulfoisophtharate dimethyl, 2 and 4, 5-trichlorobenzene sulfonic-acid dichlorophenyl, And aromatic series sulfonic acids, such as 4'-[1, 4, 5, 6, 7, 7'-hexa chloro bicyclo-[2, 2, 1]-hept-5-en -, and - IRU] benzenesulfonic acid, etc. are mentioned.

[0075] As an organic carboxylic acid, a hexane carboxylic acid, a heptane carboxylic acid, an octane carboxylic acid, a perfluoro methane carboxylic acid, a perfluoro ethane carboxylic acid, a perfluoro propane carboxylic acid, a perfluoro butane carboxylic acid, a perfluoro methyl butane carboxylic acid, a perfluoro hexane carboxylic acid, a

perfluoro heptane carboxylic acid, a perfluoro octane carboxylic acid; etc. are mentioned, for example.

[0076] As organophosphate, JI (p-t-buthylphenyl) phosphoric ester, JI (p-cumyl phenyl) phosphoric ester, JI (bromination phenyl) phosphoric ester, etc. are mentioned, for example.

[0077] On the other hand, sodium, a potassium, a lithium, caesium, etc. are mentioned as an alkali metal, and magnesium, calcium, strontium, barium, etc. are mentioned as an alkaline earth metal.

[0078] (C) As the organic alkali-metal salt and the organic alkaline-earth-metal salt of a component, it is specifically the alkali-metal salt of an organic sulfonic acid, the alkali-metal salt of organophosphate, the alkali-metal salt of an organic carboxylic acid, the alkaline-earth-metal salt of an organic sulfonic acid, the alkaline-earth-metal salt of organophosphate, and the alkaline-earth-metal salt of an organic carboxylic acid, and the salt of sodium, such as an organic sulfonic acid, organophosphate, and an organic carboxylic acid, a potassium, and caesium is especially suitable.

[0079] In the resin constituent of this invention, the organic alkali-metal salt and alkaline-earth-metal salt of the (C) component may be used by the one-sort independent, and may be used combining two or more sorts. Moreover, the loadings of the organic alkali-metal salt which is the (C) component, or an alkaline-earth-metal salt are 0.01 - 50 weight section to the (A) resin 100 weight section. If this amount exceeds 50 weight sections, while the physical properties of aromatic series polycarbonate resin are spoiled, it will become disadvantageous economically. On the contrary, if it becomes less than the 0.01 weight sections, the fire retardancy of a resin constituent or a Plastic solid will fall.

[0080] In this invention, the desirable loadings of the organic alkali-metal salt which is the (C) component, or an alkaline-earth-metal salt are the range of 0.05 - 20 weight section from the field of resin physical properties and economical efficiency to the (A) component 100 weight section.

[0081] As organopolysiloxane of the (C) component used by this invention, a phenyl content siloxane compound etc. is mentioned, for example. A Pori (methylphenyl) siloxane-polycarbonate copolymer, an others and phenyl content siloxane-polycarbonate copolymer, for example, a Pori (diphenyl) siloxane-polycarbonate copolymer, the copolymer which has the polycarbonate block guided from the phenyl content siloxane and an aromatic series polycarbonate block are included by the phenyl content siloxane compound. [compounds /, such as for example, the Pori (diphenyl) siloxane and the Pori (methylphenyl) siloxane (= methylphenyl silicon) / phenyl content siloxane] These copolymers are more specifically indicated by JP,63-289059,A, JP,1-210462,A, JP,4-202465,A, etc., and a thing can be widely used for them.

[0082] (C) It is usually good 0.01 - 50 weight section and for the organopolysiloxane of a component to carry out 0.05-20 weight section combination preferably to the (A) component 100 weight section. If there are more loadings of organopolysiloxane than 50 weight sections, the transparency of aromatic series polycarbonate resin will be lost, and the physical properties of this resin will also be spoiled. On the contrary, if it becomes less than the 0.01 weight sections, the fire retardancy of a resin constituent or a Plastic solid will fall.

[0083] In this invention, as a (C) component, an organic alkali-metal salt and an organic alkaline-earth-metal salt may be used independently, and organopolysiloxane may be

used independently, or these may be used together. The well-known additive usually used for flameproofing in addition to the above (A), (B), and the (C) component can also be used for the resin constituent of other component this inventions in the range which does not check the original transparency of aromatic series polycarbonate resin, combining it suitably.

[0084] If the transparency of aromatic series polycarbonate resin is usually held, the additive for flameproofing There is especially no limit and it can use a well-known thing widely conventionally. For example, the zinc oxide of the shape of a detailed particle, Metallic oxides, such as tin oxide, ferrous oxide, molybdenum oxide, copper oxide, and a manganese dioxide; An aluminum hydroxide, Metal hydroxides, such as a magnesium hydroxide processed with a magnesium hydroxide, zirconium hydroxide, the aluminum hydroxide that carried out oxalic acid processing, and the nickel compound; A sodium carbonate, Antimony compounds, such as a calcium carbonate, a barium carbonate, an antimony trioxide, antimony tetroxide, antimony pentoxide, and sodium antimonate, etc. can be mentioned. Moreover, chlorinated paraffin, par chloro cyclo pentadecane, tetrabromobisphenol A, Tetrabromobisphenol A epoxy oligomer or a polymer, Screw (TORIBUROMO phenoxy) Organic chlorine or bromine compounds, such as ethane and bis(tetra-bromine FUTARU imino) ethane; [Trimethyl phosphate,] Triethyl phosphate, tributyl phosphate, trioctylphosphate, Tributoxyethyl phosphate, diisopropylphenyl phosphate, Octyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, Trixylyl phosphate, cresyl diphenyl phosphate, xylyl diphenyl phosphate, Phosphoric ester, such as TORIRUJI xylyl phosphate and (2-ethylhexyl) diphenyl phosphate; Hydroxyl-group content phosphoric ester, Resorcinol screw (diphenyl) Phosphate and hydroquinone screw (diphenyl) Phosphate, Bisphenol-A screw (diphenyl) Phosphate, resorcinol screw (JIKISHIRIRU) Phosphate, Hydroquinone screw (JIKISHIRIRU) Phosphate, bisphenol-A bis(JITORIRU) phosphate, Condensed-phosphoric-acid ester compounds, such as biphenol bis(JIKISHIRIRU) phosphate and bisphenol-A bis(JIKISHIRIRU) phosphate; Red phosphorus, A halogen content phosphoric ester compound, a halogen content condensed-phosphoric-acid ester compound, The phosphine oxide compounds, such as a phosphonate compound, triphenylphosphine oxide, and tritolyl phosphine oxide; A melamine, A melamine SHIANU rate, melamine phosphate, MERAMU, MEREMU, a melon, SAKUSHINO guanamine, guanidine sulfamate, an ammonium sulfate, Nitrogen content compounds, such as ammonium phosphate, ammonium polyphosphate, and alkylamine phosphate; graphite, such as silicon compounds, such as boron compounds, such as zinc borate, metaboric acid barium, and ammonium borate, and a silica, and thermal-expansion nature, etc. can be used.

[0085] These additives may be used by the one-sort independent, and two or more sorts may be combined and they may be used.

[0086] Moreover, it can add to the resin constituent of this invention, combining suitably the class which does not check the property of this resin constituent if needed further and the various resin additives of an amount, a filler, other synthetic resin, elastomers, etc. As various resin additives, an ultraviolet ray absorbent, light stabilizer, an antioxidant, a protection-from-light agent, metal deactivator, a quencher, a heat-resistant stabilizer, lubricant, a release agent, a coloring agent, an antistatic agent, an antioxidant, a plasticizer, an impact strength amelioration agent, a compatibilizer, etc. are mentioned, for example.

[0087] In various resin additives, the ultraviolet ray absorbent of the oligomer and the polymer system which have a benzotriazol system, a benzophenone system, a salicylate system, an oxalic acid anilide system, a diphenyl cyanoacrylate system, triazine systems, and these frames, and the ultraviolet ray absorbent of an inorganic system which consists of an ultrafine particle can be mentioned as an ultraviolet ray absorbent, for example.

[0088] for example, as a benzotriazol system ultraviolet ray absorbent 2-[2'-hydroxy-5'-(hydroxymethyl) phenyl]-2H-benzotriazol, 2-[2'-hydroxy-5'-(hydroxyethyl) phenyl]-2H-benzotriazol, 2-[2'-hydroxy-3'-methyl-5'-(hydroxyethyl) phenyl]-2H-benzotriazol, 2-[2'-hydroxy-3'-t-butyl-5'-(hydroxyethyl) phenyl]-2H-benzotriazol, 2-[2'-hydroxy-3'-t-butyl-5'-(hydroxyethyl) phenyl]-5-chloro-2H-benzotriazol, 2 and 2'-methylenebis [a 6-(5-chloro-2H-benzotriazol-2-IRU)-4-(2-hydroxyethyl) phenol], 2 and 2'-methylenebis [a 6-(2H-benzotriazol-2-IRU)-4-(3-hydroxypropyl) phenol], 2 and 2'-methylenebis [a 6-(5-chloro-2H-benzotriazol-2-IRU)-4-(3-hydroxypropyl) phenol], 2 and 2'-methylenebis [a 6-(2H-benzotriazol-2-IRU)-4-(2-hydroxypropyl) phenol], 2 and 2'-methylenebis [a 6-(5-chloro-2H-benzotriazol-2-IRU)-4-(2-hydroxypropyl) phenol], 2 and 2'-methylenebis [a 6-(5-chloro-2H-benzotriazol-2-IRU)-4-(4-hydroxy butyl) phenol], 6-(2H-benzotriazol-2-IRU)-4-(2-hydroxyethyl) phenol] ether, 2, and 2' bis[-] [6-(2H-benzotriazol-2-IRU)-4-(2-hydroxyethyl) phenol] sulfone etc. is mentioned.

[0089] As a triazine system ultraviolet ray absorbent, for example 2-(2, 4-dihydroxy phenyl)-4, 6-diphenyl-s-triazine, 2-(2, 4-dihydroxy phenyl)-4, 6-bis(2, 4-dimethylphenyl)-s-triazine, 2-(2, 4-dihydroxy phenyl)-4, 6-bis(2, 4-dimethoxy phenyl)-s-triazine, 2-(2-hydroxy-4-(2-hydroxyethyl) phenyl)-4, 6-bis(2-hydroxy-4-dimethylphenyl)-s-triazine, 2-(2-hydroxy-4-(2-hydroxyethyloxy) phenyl)-4, 6-bis(2-hydroxy-4-dimethylphenyl)-s-triazine, 2-(2-hydroxy-4-(3-hydroxy propyloxy) phenyl)-4 and 6-bis(2-hydroxy-4-dimethylphenyl)-s-triazine etc. is mentioned.

[0090] As an antioxidant, a phenolic antioxidant, a sulfur system antioxidant, the Lynn system antioxidant, etc. can be mentioned, for example.

[0091] As a phenolic antioxidant, for example 2, 6-G tert-butyl-4-methyl phenol, Pentaerythrityl tetrakis [3-(3' and 5'-G tert-butyl-4'-hydroxyphenyl)-propionate], Octadecyl -3 -(3' and 5'-G tert-butyl-4'-hydroxyphenyl)- Propionate, 2,2'-methylene bis (4-methyl-6-tert-butylphenol), 2,2'-methylene bis (4-ethyl-6-tert-butylphenol), 4 and 4'-butylidenebis (3-methyl-6-tert-butylphenol), 4,4'-thiobis (3-methyl-6-tert-butylphenol), 2 4-screw-(normal-octylthio)-6-4"-hydroxy - 3' and 5'-G tert-butylanilino-1,3,5-triazine, A 2 and 2-thio-diethylene screw [3-(3' and 5'-G tert-butyl-4'-hydroxyphenyl)-propionate], N and N'-hexa methylenebis (3 5-G tert-butyl-4-hydroxy hydronalium thinner MAMIDO), 3 and 9-{2-[3-(3-butyl-4-hydroxy-5-methylphenyl) propionyloxy]-1 and 1-dimethylethyl}-tetraoxaspiro [2, 4, 8, and 10-] [5, 5] undecane etc. can be mentioned.

[0092] As a sulfur system anti-oxidant, for example Dilauryl-3,3'-thiodipropionate, JITORIDESHIRU -3, 3'-thiodipropionate, dimyristyl -3, 3'-thiodipropionate, Distearyl -3, 3'-thiodipropionate, pentaerythrityl-tetrakis (3-mercaptopropionate), pentaerythrityl-tetrakis (3-laurylthio propionate) and a screw -- {-- 2-methyl-4-{3-normal-alkyl (C12 --) Or a C14 thio propionyloxy}-5-tert-buthylphenyl} sulfide, 2-mercapto Benz imidazole, glycerol-3-stearyl thiopropionate, etc. can be mentioned.

[0093] As a Lynn system antioxidant, tris (nonylphenyl) phosphite, triphenyl phosphite, tris (2, 4-G tert-buthylphenyl) phosphite, diphenyl isodecyl phosphite, diphenyl isooctylphosphite, distearylpentaerythrityldiphosphite, JI (2, 4-G tert-buthylphenyl)

pentaerythritoldiphosphite, tetrakis (2, 4-G tert-buthylphenyl) -4, 4-BIFENIREJIHOSUHO night, etc. can be mentioned, for example.

[0094] As light stabilizer, for example 2-(2-hydroxy-5-tert-octyl phenyl) benzotriazol, 2-(3-tert-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzo triazole, 2-(5-methyl-2-hydroxyphenyl) benzotriazol, 2-[2-hydroxy-3 and 5-bis(alpha and alpha-dimethylbenzyl) phenyl]-2H-benzotriazol, A 2,2'-methylene bis (4-cumyl-6-benzotriazol phenyl), 2, and 2'-p-phenylene screw (3, 1-benzoxazine-4-ON), polyalkylene naphthalate, etc. are mentioned.

[0095] As a filler, for example A mica, a kaolin, talc, a silica, clay, A calcium carbonate, a calcium sulfate, calcium silicate, a glass bead, Glass balun, a glass flake, a glass fiber, an alumina, titanium oxide, Fibrous titanic-acid alkali metal, a fibrous boric-acid transition-metals salt, a fibrous boric-acid alkaline-earth-metal salt, A zinc oxide whisker, a titanium oxide whisker, a magnesium-oxide whisker, A gypsum-fibrosus whisker, an aluminum silicate whisker, a calcium silicate whisker, A silicon carbide whisker, a titanium carbide whisker, a silicon nitride whisker, a titanium nitride whisker, a carbon fiber, an alumina fiber, an alumina-silica fiber, a zirconia fiber, a quartz fiber, a metal fiber, etc. are mentioned.

[0096] Various above-mentioned additives and an above-mentioned filler may be used independently, or two or more sorts may use them, mixing.

[0097] As other synthetic resin and elastomers, when it mixes with polycarbonate resin, it can be used in the range which does not check the transparency, mixing suitably. For example, the polyester which consists of aromatic series dicarboxylic acid or its derivative, and a dihydric phenol or its derivative is mentioned.

[0098] It is possible to combine the compound which can secure fire retardancy or transparency as other additives further in this invention. For example, when resin burns, oxygenated oligomer which promotes carbonization of the resin or a polymer, for example, a polyethylene glycol, and BORIBI nil alcohol are mentioned. Moreover, the oligomer or the polymer which makes a basic frame oxygenated compounds, such as trimethylolethane, TORIMECHI roll butane, propane trithiol, and pentaerythritol, and these ether derivatives, an ester derivative, or said oxygenated compound is desirable. These may be used by the one-sort independent, may be combined two or more sorts and may be used.

[0099] The resin constituent of this invention can be prepared by blending and kneading each aforementioned component (A), (B) and the (C) component, and the various addition components used if needed. It can carry out to combination and kneading by the approach using the approach usually used, for example, a ribbon blender, a Henschel mixer, a V type blender, a NAUTA mixer, a Banbury mixer, a drum tumbler, a monopodium screw extruder, a twin screw extruder, a ko kneader, a multiaxial screw extruder, etc. In addition, whenever [for kneading / stoving temperature] can usually be suitably chosen in 240-300 degrees C.

[0100] Fabrication is easily possible for the fire-resistant polycarbonate resin constituent obtained thus by approaches, such as the known various shaping approaches, for example, extrusion molding, injection molding, compression molding, calender shaping, and rotational casting, and it can be applied to blow molding, a vacuum forming, gas injection shaping, etc., and can be suitably used as an ingredient of housing, such as an electron and an electric product with which the outstanding fire retardancy is demanded,

and OA equipment, or a chassis application, and various components.

[0101] Thus, the obtained resin constituent can be used for industrial fields, such as the electrical and electric equipment with which transparency is demanded, an electron, a communication link, agriculture-and-forestry fishery, mining, construction, food, fiber, clothing, medicine, coal, petroleum, rubber, leather, an automobile, a precision mechanical equipment, wood, furniture, printing, and a musical instrument. For example, a printer, a personal computer, a word processor, a keyboard, PDA (small information terminal), Telephone, facsimile, a copying machine, ECR (electronic cash register), a calculator, Office work and OA equipment, such as an electronic notebook, an electronic dictionary, a card, an electrode holder, and stationery, washing machine, a refrigerator, a cleaner, a microwave oven, lighting fitting, a game machine, an iron, Household-electric-appliances devices, such as a kotatsu, TV and VTR, a video camera, a digital camera, It is used for the application of the electrical and electric equipment and electronic parts, such as AV equipments, such as a radio cassette recorder, a tape recorder, a mini disc, a CD player, PD and DVD, a loudspeaker, and a liquid crystal display, a connector, a switch, a cable, and a clock, communication equipment, etc. Moreover, a seat, belts (packing, frontal land, etc.), a head-lining flare, the compatible top, An armrest, a door trim, a rear package tray, a carpet, a mat, A sun visor, foil covering, mattress covering, an air bag, an insulating material, hanging -- a hand -- hanging -- ****, electric-wire clothing material, electric insulation material, a coating, and a coating material -- Upper flare material, flooring, ****, a deck panel, coverings, a plywood, a crown plate, a diaphragm, A side attachment wall, a carpet, wallpaper, a wall covering material, a sheathing material, interior material, roofing, an acoustical insulation board, Automobiles, such as a heat insulation plate and aperture material, a car, a vessel, the aircraft and a structural ingredient, and clothing, The application of a life and sport leisure goods, such as a curtain, a sheet, a plywood, a synthetic fiber plate, a carpet, a door mat, a sheet, a bucket, a hose, a container, glasses, a bag, a case, goggles, a ski outfit, a racket, tentorium, a musical instrument, and a toy, is mentioned.

[0102]

[Example] Although an example and the example of a comparison are hung up and this invention is clarified further hereafter, this invention is not limited to these. In addition, evaluation of a resin constituent was performed by the following approach.

[0103] Fire retardancy: Beforehand, the (B) component, the (C) component, and other components were requirements-added, 110 degrees C was mixed with the polycarbonate resin ((A) component) which carried out predrying for 10 hours, the twin screw extruder (S1-KRC 25mm Kneader: Kurimoto Make) was used, and it kneaded and pelletized with the cylinder temperature of 270 degrees C, and the nozzle temperature of 260 degrees C.

[0104] the obtained pellet -- 110 degrees C -- after 10-hour desiccation and injection molding machine (MINIMAT-26/15B --) The Sumitomo Heavy Industries, Ltd. make is used. With the cylinder temperature of 280 degrees C, and the die temperature of 70 degrees C A Plastic solid with the thickness of 1/16 inch (about 1.6mm), a width of face [of 12.5mm], and a die length of 127mm is fabricated. The method of examining UL-94V () [Test for] Flammability of Plastic Materials for Parts in Devices and Appliances Fire-resistant evaluation was performed according to UL 94 and Fourth Edition.

[0105] Average burn time: The number of framing sum total seconds after a total of every 2 times ten approaching flames showed said fire-resistant trial to one-set five test

pieces.

[0106] Drip: In said fire-resistant trial, the approaching flame was carried out to five test pieces a total of 10 times, and the count of the framing grain (drip) which ignites the cotton under 30cm was measured at the time of a combustion test.

[0107] HAZE: Like the case of the above and fire-resistant evaluation, fabricate a test piece with the thickness of 3mm, a width of face [of 50mm], and a die length of 90mm, and it is JIS. It applies to K-7105-1981 correspondingly, and is HAZE. METER (trade name: HAZE METER NDH 2000, Nippon Denshoku Industries Co., Ltd. make) It used, HAZE (%) was measured and it considered as the index of transparency.

[0108] synthetic example 1 The synthetic H.R.Allcock work of phenoxy phosphazene ($[N=P(-O-Ph)_2]$ 3 and $[N=P(-O-Ph)_2]$ it abbreviates to "FR-1" the mixture of 4, and the following.), and "Phosphorus-Nitrogen Compounds -- " -- Academic FR-1 was manufactured according to Press, (1972), and the approach indicated by 151.

[0109] Namely, after adding the toluene solution of a sodium phenolate in 580g of 20% chlorobenzene solutions containing a dichlorophosphazene oligomer (62% [of trimers], mixture of 38% of tetramers) 1.0 unit mol (115.9g) under stirring, it reacted to them at 110 degrees C for 10 hours. The residual chlorinity of a product is <0.01% and checked that they were the following compounds.

[0110] $[N=P(-O-Ph)_2]$ 3, example 2 of 4 composition The toluene solution of a sodium phenolate was prepared by carrying out the heating reflux of the phenol of 1.1 mols (103.5g) of composition of the phenoxy phosphazene compound (it abbreviates to "FR-2" hereafter.) which has the structure of cross linkage by PARAFENIREN, a 1.1 mols (44.0g) sodium hydroxide, 50g of water, and the toluene 500ml mixture, and removing only water besides a system.

[0111] The toluene solution of the lithium salt of hydroquinone and a phenol was prepared by putting 0.15 mols (16.5g) hydroquinone, a 1.0 mols (94.1g) phenol, a 1.3 mols (31.1g) lithium hydroxide, 52g of water, and toluene 600ml mixture into a 2l. 4 opening flask, carrying out heating reflux in parallel to said reaction, and removing only water besides a system. After 580g of 20% chlorobenzene solutions which contain a dichlorophosphazene oligomer (72% [of trimers], 15% [of tetramers], pentamer and 8% [of hexamers], 3% [of 7 ****], and more than octamer 2% of mixture) 1.0 unit mol (115.9g) in this toluene solution was dropped below 30 degrees C under stirring, the stirring reaction was carried out at 110 degrees C for 4 hours. Next, after adding under stirring the toluene solution of a sodium phenolate prepared previously, the reaction was continued at 110 degrees C for 8 hours.

[0112] After 1l. of sodium-hydroxide water solutions washed the reaction mixture 3 times 3% after reaction termination, next 1l. of water washed 3 times, the organic layer was condensed under reduced pressure. Concentration hardening by drying of the obtained product was carried out by 80 degrees C and 266Pa or less, and 211g white powder was obtained.

[0113] The hydrolysis chlorine of the bridge formation phenoxy phosphazene compound obtained above was 0.01% or less, and the presentation of the last object was $[N=P(-O-p-Ph-O-) 0.15 (-O-Ph) 1.7]$ from the CHN elemental-analysis value at the Lynn content list.

[0114] Weight average molecular weight (Mw) was 1100 in polystyrene conversion (based on GPC analysis), TG/DTA analysis did not show the clear melting point, but 306 degrees C and 5% weight reduction temperature of decomposition initiation temperature

were 311 degrees C.

[0115] Moreover, as a result of performing the quantum of a residual hydroxy group by the acetylating method, it was below limit of detection (considering as the hydroxy equivalent per sample $1\text{g} : 1 \times 10^{-6}\text{Eq}/(\text{g})$ or less).

Synthetic example 3 0.7 mol [of synthetic phenol of a phenoxy phosphazene compound (it abbreviates to "FR-3" hereafter.)] (65.9g) and toluene 500ml which has the structure of cross linkage by the 2 and 2-bis(p-oxy-phenyl) isopropylidene radical was put into the 1l. 4 opening flask, and under stirring, keeping internal solution temperature at 25 degrees C, the metallic-sodium 0.65 gram atom (14.9g) was cut out finely, and was thrown in. Stirring was continued for 8 hours until metallic sodium disappeared completely at 77-113 degrees C after injection termination.

[0116] It is concurrent with said reaction and bisphenol A. 0.25-mol (57.1g), 1.1 mol [of phenols] (103.5g), and tetra-HIDORU furan (THF) 800ml was put into the 3l. 4 opening flask, and under stirring, keeping internal solution temperature at 25 degrees C, the metal lithium 1.6 gram atom (11.1g) was cut out finely, and was thrown in. Stirring was continued for 8 hours after injection termination until the metal lithium disappeared completely at 61-68 degrees C. Under stirring of 386g of 30% chlorobenzene solutions which contain a dichlorophosphazene oligomer (72% [of trimers], 15% [of tetramers], pentamer and 8% [of hexamers], 3% [of 7 ****], and more than octamer 2% of mixture) 1.0 unit mol (115.9g) in this slurry solution, after being dropped over 1 hour, keeping internal solution temperature at 20 degrees C or less, it reacted at 80 degrees C for 4 hours. Subsequently, under stirring, after adding the sodium-phenolate solution prepared separately over 1 hour, keeping internal solution temperature at 20 degrees C, it reacted at 80 degrees C for 10 hours.

[0117] After reaction termination, the reaction mixture was condensed and 1l. of toluene was newly added except for THF. It is 2%NaOH about this toluene solution. After it washed 3 times by 1l., next 1l. of water washed 3 times, the organic layer was condensed under reduced pressure. Concentration hardening by drying of the obtained product was carried out by 80 degrees C and 266Pa or less, and 230g white powder was obtained.

[0118] The hydrolysis chlorine of the bridge formation phenoxy phosphazene compound obtained above was 0.01% or less, and the presentation of the last object was $[\text{N}=\text{P}(-\text{O}-\text{Ph}-\text{C}(\text{CH}_3)_2-\text{Ph}-\text{O}-)]_{0.25}(-\text{O}-\text{Ph})_{1.50}$ from the CHN elemental-analysis value at the Lynn content list.

[0119] Weight average molecular weight (M_w) was 1140 in polystyrene conversion (based on GPC analysis), TG/DTA analysis did not show the clear melting point, but 310 degrees C and 5% weight reduction temperature of decomposition initiation temperature were 315 degrees C.

[0120] Moreover, as a result of performing the quantum of residual hydroxyl by the acetylating method, it was below limit of detection (considering as the hydroxyl equivalent per sample $1\text{g} : 1 \times 10^{-6}\text{Eq}/(\text{g})$ or less).

Synthetic example 4 0.4 mol [of synthetic phenol of the phenoxy phosphazene (it abbreviates to "FR-4" hereafter.) which has the structure of cross linkage by 4 and 4-sulfonyl diphenylene (bisphenol-S residue)] (37.6g), and tetrahydrofuran (THF) 500ml was put into the 1l. 4 opening flask, and under stirring, keeping internal solution temperature at 25 degrees C, the metallic-sodium 0.45 gram atom (9.2g) was cut out finely, and was thrown in. Stirring was continued for 5 hours until metallic sodium

disappeared completely at 65-72 degrees C after injection termination.

[0121] It is concurrent with said reaction and they are 1.70 mols (160.0g) of phenols, and a bisphenol with a 1l. 4 opening flask. - S 0.05 mols (12.5g) were dissolved in THF500ml, the metallic-sodium 1.8 gram atom (41.4g) was thrown in below 25 degrees C, stirring was continued at a temperature up and 61 degrees C - 68 degrees C to 61 degrees C over 1 hour for 6 hours after injection termination, and the sodium-phenolate mixed solution was prepared. The stirring reaction of this solution was carried out at 71-73 degrees C after dropping under cooling / stirring of 25 degrees C or less for 5 hours at 580g of 20% chlorobenzene solutions containing a dichlorophosphazene oligomer (72% [of trimers], 15% [of tetramers], pentamer and 8% [of hexamers], 3% [of 7 ****], and more than octamer 2% of mixture) 1.0 unit mol (115.9g). Next, after the sodium-phenolate mixed solution prepared previously was dropped, the reaction was continued at 71-73 degrees C for 10 hours.

[0122] After condensing the reaction mixture after reaction termination and remelting to chlorobenzene 500ml, sulfuric acid treatment, 5% sodium bicarbonate backwashing by water, and three rinsings were performed 3 times and 5%, concentration hardening by drying of the 5%NaOH backwashing by water was carried out by 266Pa or less, and 220g of white solid-states was obtained.

[0123] The hydrolysis chlorine of the bridge formation phenoxy phosphazene compound obtained above is 0.01% or less, and the presentation of this object was mostly determined as $[N=P(-O-Ph-SO_2-Ph-O-) 0.05 (-O-Ph) 1.90]$ from the CHN elemental-analysis value at the phosphorus content list.

[0124] Weight average molecular weight (Mw) was 1070 in polystyrene conversion, and the melting out temperature (Tm) by TG/DTA analysis was [334 degrees C and 5% weight reduction temperature of 103 degrees C and decomposition initiation temperature] 341 degrees C.

[0125] Moreover, as a result of performing the quantum of a residual hydroxy group by the acetylating method, it was below limit of detection (considering as the hydroxy equivalent per sample 1g : $1 \times 10^{-6} \text{Eq/(g)}$ or less).

[0126] example 1 polycarbonate resin (trade name: -- a you pyrone and S-2000F --) Viscosity average molecular weight : 22,900, the 100 weight sections by Mitsubishi Engineering, The FR-12.5 weight section and a perfluoro butane sulfonic-acid potassium (It abbreviates to "C-1" hereafter) After carrying out the dryblend of the 0.2 weight sections beforehand, this invention resin constituent of a pellet type was obtained by supplying and carrying out melting extrusion of the cylinder temperature to the hopper of the biaxial extruder set as 270 degrees C (the Wako Pure Chem Industries make).

[0127] this invention resin constituent was obtained like the example 1, respectively except having changed FR-1 in two to example 4 example 1 into FR-2, FR-3, or FR-4.

[0128] Except having changed C-1 in five to example 8 example 1 into methylphenyl silicon (trade name: TSF-4300, Toshiba Silicone, Inc. make) (it abbreviating to "C-2" hereafter), it blended as shown in Table 1, and this invention resin constituent was obtained like the example 1, respectively.

[0129] this invention resin constituent was obtained like the example 1, respectively except having added trimethylolthane (it abbreviating to "D-1" the Wako Pure Chem Industries make and the following) to the combination in nine to example 10 example 1, and an example 5.

[0130] The resin constituent was obtained like the example 1, respectively except having changed as the example 1 of a comparison - 3 each compounding agent were shown in Table 1.

[0131] The loadings (loadings to the (A) component 100 weight section (weight section)) of the (B) component in the above-mentioned examples 1-10 and the examples 1-3 of a comparison, the (C) component, and other components are shown in Table 1, and those evaluation results are shown in Table 2, respectively.

[0132]

[Table 1]

		(B)成分				(C)成分		D-1
		FR-1	FR-2	FR-3	FR-4	C-1	C-2	
実施例	1	2.50	—	—	—	0.20	—	—
	2	—	2.50	—	—	0.20	—	—
	3	—	—	2.50	—	0.20	—	—
	4	—	—	—	2.50	0.20	—	—
	5	2.50	—	—	—	—	0.30	—
	6	—	2.50	—	—	—	0.30	—
	7	—	—	2.50	—	—	0.30	—
	8	—	—	—	2.50	—	0.30	—
	9	2.50	—	—	—	0.20	—	1.00
	10	2.50	—	—	—	—	0.30	1.00
比較例	1	—	—	—	—	0.20	—	—
	2	—	—	—	—	—	0.30	—
	3	—	—	—	—	0.20	—	1.00

[0133]

[Table 2]

		難燃性 UL-94	フレイミング 合計秒数(秒)	ドリップ回数 (回)	透 明 性 HAZE (%)
実施例	1	V-0	4	0	5.4
	2	V-0	3	0	3.1
	3	V-0	2	0	2.0
	4	V-0	6	0	4.9
	5	V-0	4	0	3.8
	6	V-0	1	0	2.3
	7	V-0	3	0	3.0
	8	V-0	3	0	4.2
	9	V-0	2	0	2.0
	10	V-0	2	0	2.2
比較例	1	V-1	70	0	6.5
	2	V-1	63	0	5.1
	3	V-1	85	0	5.3

[0134]

[Effect of the Invention] Without a polycarbonate spoiling the transparency and the physical properties which it originally has, the fire-resistant polycarbonate resin constituent of this invention can prevent dropping at the time of combustion, and may discover high fire retardancy. Therefore, the fire-resistant polycarbonate resin constituent

of this invention is suitably used as materials, such as various kinds of mold goods, for example, the electrical and electric equipment and electronic parts, OA machine vessel part article, an automobile and a machine part, and building materials.

[Translation done.]